







# Missione 4 Istruzione e Ricerca

## **ATHENA**

A novel approach Towards the management of building materials of particular Historical-artistic interest: assessment of the radon Exhalation and the radiological risk due to Natural radioActivity content

(PNRR - Missione 4, Componente 2, Investimento 1.1 - Bando Prin 2022 PNRR -Decreto Direttoriale n. 1409 del 14-09-2022)

CUP J53D23014560001 - codice identificativo P2022CPA2K









# Which target?

The main target of the ATHENA project is to define an innovative protocol for the systematic characterisation of construction materials used in buildings of particular historical and artistic interest, particularly in terms of radon gas exhalation rates.



# Why it is important what we do

The development of ad-hoc techniques and protocols for the quantitative assessment of the natural radioactivity content in building materials, pre- and post-treatment (ageing, consolidation) can play a key role in the field of cultural heritage, considering that materials potentially enriched with radionuclides of natural origin have been used in the past to construct monuments of particular historical and artistic interest.









## The research group

#### **Unit 1 – University of Messina**(68.707 Euro)

Caridi Francesco (P.I.) <a href="https://unime.unifind.cineca.it/get/person/026777">https://unime.unifind.cineca.it/get/person/026777</a>
Venuti Valentina <a href="https://unime.unifind.cineca.it/get/person/010171">https://unime.unifind.cineca.it/get/person/010171</a>
Majolino Domenico <a href="https://unime.unifind.cineca.it/get/person/009121">https://unime.unifind.cineca.it/get/person/010171</a>

#### Unit 2 – University "Mediterranea" of Reggio Calabria (56.077 Euro)

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#### Unit 3 – University of Salerno (31.663 Euro)

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#### Unit 4 – University of Calabria (21.336 Euro)

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#### Unit 5 – University of Cagliari (28.966 Euro)

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## **Skills**

The five research units (RUs) involved in the ATHENA project constitute a 'scientific' network with complementary expertise,

- including sampling of cultural heritage building materials, assessment of radon exhalation rates, mineralogy and radiological risk assessment due to natural radioactivity content, up to accelerated ageing, treatment with consolidants and assessment of radon exhalation after treatments.
- The team is well-mixed in that it combines the expertise of the ATHENA project PI in the field of radiological risk assessment due to radioactivity content in environmental samples with that of the other participants, experts in, among others:
- products and procedures for the conservation of stone materials belonging to the Built Heritage;
- assessment of radon gas exposure and exhalation rates in the context of cultural heritage;
- structural and physico-chemical characterisation of materials, including those of particular historical and artistic interest.

The synergy between all components of the ATHENA project can guarantee a favourable outcome of the project itself, with a high impact in the field of environmental quality, in particular for a better protection of historical sites and monuments.









## **Milestones**

#### **MILESTONE 1**

To assess any possible radiological risk for the human beings related to outdoor exposure to gamma rays from building materials of interest in the field of cultural heritage.

#### **MILESTONE 2**

To identify the most effective long-stable consolidating agent which minimize the radon exhalation rate while maintaining high compatibility with the substrate, in view of a rationalized selection of a restoration procedure to be applied to building materials.

#### **MILESTONE 3**

To clarify the correlation between the fundamental properties of the investigated building stones and the calculated radon exhalation rates, in order to improve the indoor environmental air quality.









#### Milestone 1

ACTIVITY	ASSIGNED	SIGNED I year II yea										nar .				
	то	BIM.	BIM.	BIM.	BIM.	BIM. 5	BIM.	BIM.	BIM. 2	BIM. 3	BIM.	BIM. 5	BIM.			
Sampling	RUFFOLO S	х	х													
Mineralogy and radiological risk assessment due to the natural radioactivity content	CARIDI F FAGGIO G			х	x	х	х	х	x							

The **first milestone** of the ATHENA project, to be achieved by the 16<sup>th</sup> month of the project (February 2025), is associated with the following deliverables:

**Deliverable 1.1:** Measurement of the specific activity of the naturally occurring radioactive elements, such as Ra-226, Th-232 and K-40, contained in the investigated building materials by using High Purity Germanium (HPGe) gamma-ray spectrometry and assessment of any possible radiological risk for the human beings through the calculation of the following indexes: activity concentration index (I), alpha index (I $\alpha$ ), absorbed gamma dose rate (D), radium equivalent activity (Ra<sub>eq</sub>), hazard indexes (H<sub>in</sub> and H<sub>ex</sub>), annual effective dose equivalent outdoor (AEDE<sub>out</sub>) and excess lifetime cancer risk (ELCR).

A Technical Report of the obtained results will be released upon completion, by the 16th month of the ATHENA project.

**Deliverable 1.2:** Identification of the main radioisotope-bearing minerals responsible of the naturally occurring radionuclides present in the investigated samples (Technical Report of the obtained results) through X-ray Diffraction (XRD) and Micro-Raman Scattering (MRS) measurements.

A Technical Report of the obtained results will be released upon completion, by the 16th month of the ATHENA project.









#### Milestone 2

ACTIVITY	ASSIGNED			I y	ear			II year					
	то	BIM.	BIM.	BIM. 3	BIM.	BIM. 5	BIM.	BIM.	BIM.	81M. 3	BIM.	BIM.	BIM 6
Sampling	RUFFOLO S	х	х										
Assessment of the radon exhalation rate before treatment	GUIDA M DA PELO S		×	х	х	х							
Accelerated aging, treatment with consolidant and evaluation of the radon exhalation	GUIDA M RUFFOLO S DA PELO S			×	×	×	×	×	×	х	x	×	

The **second milestone** of the ATHENA project, to be achieved by the 22<sup>nd</sup> month of the project (September 2025), is associated with the following deliverables:

**Deliverable 2.1:** Assessment of the radon exhalation rate for the untreated investigated cultural heritage building materials by using the Closed Chamber Method (CCM).

A Technical Report of the obtained results will be released upon completion, by the 9<sup>th</sup> month of the ATHENA project.

**Deliverable 2.2:** Evaluation of the radon exhalation by using the CCM after laboratory treatments of the investigated materials, i.e. accelerated aging tests together with consolidation through the use of different selected commercially-available consolidants. A Technical Report of the obtained results will be released upon completion, by the 22<sup>nd</sup> month of the ATHENA project.









#### Milestone 3

ACTIVITY	ASSIGNED TO	L		Iy	ear			II year								
		BIM. 1	BIM. 2	BIM. 3	BIM. 4	BIM. 5	BIM. 6	BIM. 1	BIM. 2	BIM. 3	BIM. 4	BIM. 5	BIM.			
Sampling	RUFFOLO S	х	х													
Laboratory-treated samples characterization	CARIDI F RUFFOLO S			х	×	х	х	×	х	×	×	×				

The **third milestone** of the ATHENA project, to be achieved by the 22<sup>nd</sup> month of the project (September 2025), is associated with the following deliverables:

**Deliverable 3.1:** Evaluation of the porosity, roughness, crystalline abundance, penetration depth of consolidant products, and other petrographical and textural features of the laboratory-treated construction materials through Scanning (SEM) Electron Microscopy, also associated with Energy Dispersive X-rays spectroscopy (EDX).

A Technical Report of the obtained results will be released upon completion, by the 18th month of the ATHENA project.

**Deliverable 3.2:** Characterization of the laboratory-treated building materials at elemental and molecular scales through InfraRed (IR), X-Ray Fluorescence (XRF) and Raman spectroscopy and microspectroscopy.

A Technical Report of the obtained results will be released upon completion, by the 22<sup>nd</sup> month of the ATHENA project.









#### Gantt diagram

				Щ										mont						
				1	2 3	3 4	5	6	7 8	9	10 1	1 12	2 13	14 15	16	17 1	8 19	20 2	1 22	23 24
	Activity		Role of each RU																	
WP1 Leader: RU1-UniME	Administration	RU1-UniME/RU2- UniRC/RU3- UniSA/RU4- UniCS/RU5-UniCA	i) Overall project management, financial management, steering group/consortium meetings and formal reporting  i) Collection of cultural heritage building materials  i) Measurement of the radon exhalation rate																	
WP2 Leader: RU4-UniCS	Sampling	RU4-UniCS																		
WP3 Leader: RU3-UniSA	Assessment of the radon exhalation rate	RU3-UniSA RU5-UniCA																		
WP4 Leader: RU1-UniME	Mineralogy and radiological risk assessment due to the	RU1-UniME	i) Characterization by HPGe gamma spectrometry and radiological risk assessment ii) Characterization by μRaman																	
	natural radioactivity content	RU2-UniRC	i) Characterization by XRD					Т		П	Т									
	Accelerated aging, treatment with consolidant, samples	RU4-UniCS	i) Accelerated aging ii) Treatment with consolidants iii) Characterization by SEM, SEM-EDX																	
WP5 Leader: RU4- UniCS	characterization and	RU1-UniME	i) Characterization by IR, XRF and Raman																	
	evaluation of the radon exhalation	RU3-UniSA RU5-UniCA	i) Measurement of the radon exhalation rate																	
			i) Brochure/flyer, educational material, posters																	
			ii) Web-site																	
		RU1-UniME/RU2-	iii) Scientific publications																	
WP6 Leader: RU1-UniME	Leader: RU1-UniME Dissemination UniRC/RU3-UniSA/ RU4-UniCS/RU5- UniCA		iv) Strategic planning of communication, meetings among the partners, final plenary meeting																	
			v) Seminars, ex-cathedra and e-learning program																	









## **Publications**

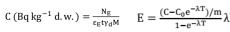
1. F. Caridi, D. Chiriu, S. Da Pelo, G. Faggio, M. Guida, G. Messina, M. Ponte, S.A. Ruffolo, D. Majolino, V. Venuti Radon exhalation rate, radioactivity content and mineralogy assessment of building materials of particular historical-artistic interest

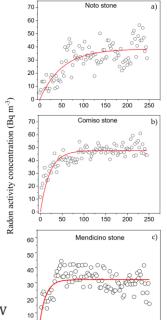
Applied Sciences, submitted











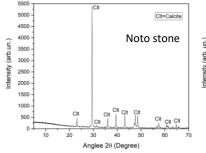
Time (h)

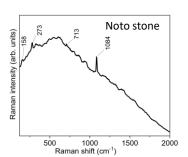
C1-	222Rn exhalation rate
Sample	(Bq h-1 kg-1)
Noto stone	$0.013 \pm 0.003$
Comiso stone	$0.040 \pm 0.006$
Mendicino stone	$0.030 \pm 0.010$

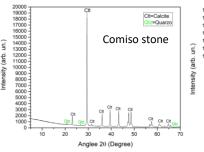
	Act	ivity concenti	ation
Sample	C <sub>Ra</sub>	$C_{Th}$	Ск
	(Bq kg-1)	(Bq kg-1)	(Bq kg-1)
Noto stone	$14.5 \pm 1.6$	$0.99 \pm 0.16$	$6.2 \pm 0.8$
Comiso stone	$21.9 \pm 1.9$	$1.8 \pm 0.3$	$3.2 \pm 0.4$
Mendicino stone	$8.6 \pm 0.7$	$9.4 \pm 0.8$	$169 \pm 23$

Sample	D (nGy h-1)	AEDE (μSv y-1)	ACI	$I_{\alpha}$
Noto stone	14.9	73.2	0.06	0.07
Comiso stone	22.4	110	0.08	0.11
Mendicino stone	31.8	156	0.13	0.04

D (nGy h<sup>-1</sup>) = 
$$0.462C_{Ra} + 0.604C_{Th} + 0.0417C_{K}$$
  
AEDE = D × 8760 h × 0.7 Sv Gy<sup>-1</sup> × 0.8 × 10<sup>-6</sup>  
ACI = ( $C_{Ra}/300 + C_{Th}/200 + C_{K}/3000$ )  
 $I_{\alpha} = C_{Ra}/200$ 





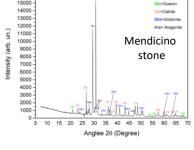


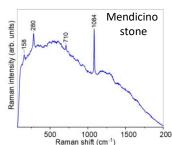
1000

Comiso stone

1500

2000













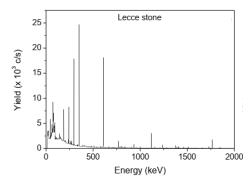
2. F. Caridi, D. Majolino, V. Venuti, D. Chiriu, S. Da Pelo, G. Faggio, G. Messina, M. Guida, M. Ponte, S.A. Ruffolo

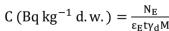
# Assessment of the radon exhalation and the radiological risk due to natural radioactivity content in the "Pietra di Lecce" building material: a case study

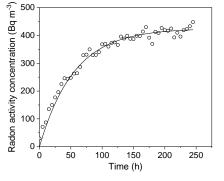
WSEAS Transactions on Environment and Development, in press











$$E = \frac{(C - C_0 e^{-\lambda T})/m}{1 - e^{-\lambda T}} \lambda V$$

	<sup>222</sup> Rn	;	Specific activi	ity
Sample	exhalation rate (Bq h <sup>-1</sup> kg <sup>-1</sup> )	C <sub>Ra</sub> (Bq kg <sup>-1</sup> d.w.)	C <sub>Th</sub> (Bq kg <sup>-1</sup> d.w.)	C <sub>K</sub> (Bq kg <sup>-1</sup> d.w.)
Pietra di Lecce	$0.156 \pm 0.019$	$163\pm27$	$0.9 \pm 0.2$	$22.4 \pm 4.6$

$D \; (nGy \; h^{\text{-}1}) = 0.462 C_{Ra} + 0.604 C_{Th} + 0.0417 C_{K}$
$ \begin{array}{l} AEDE_{out} \; (mSv \; y^{\text{-}1}) = D \; (nGy \; h^{\text{-}1}) \times 8760 \; h \times 0.7 \; Sv \\ Gy^{\text{-}1} \times 0.2 \times 10^{\text{-}6} \\ \end{array} $
AEDE $_{in}$ (mSv y-1) = D (nGy h-1) × 8760 h × 0.7 Sv Gy-1 × 0.8 × 10-6
$Ra_{eq} \left( Bq \; kg^{\text{-}1} \right) = C_{Ra} + 1.43 C_{Th} + 0.077 C_{K}$
$H_{ex} = (C_{Ra}/370 + C_{Th}/259 + C_K/4810)$
$H_{in} = (C_{Ra}/185 + C_{Th}/259 + C_K/4810)$
$I = (C_{Ra}/300 + C_{Th}/200 + C_K/3000)$

Sample	D (nGy h <sup>-1</sup> )	AEDE <sub>out</sub> (μSv y <sup>-1</sup> )	AEDE <sub>in</sub> (μSv y <sup>-1</sup> )	Ra <sub>eq</sub> (Bq kg <sup>-1</sup> )	Hex	H <sub>in</sub>	I	$I_{\alpha}$
Pietra di	76.8	94.2	377	166	0.4	0.9	0.6	0.82
Lecce								





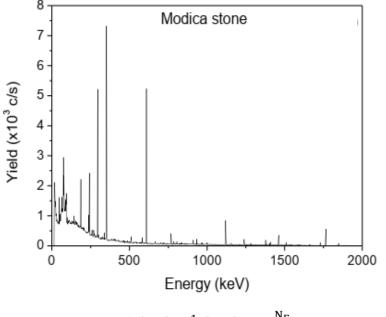




3. F. Caridi, D. Chiriu, S. Da Pelo, G. Faggio, M. Guida, D. Majolino, G. Messina, M. Ponte, S.A. Ruffolo, V. Venuti Natural radioactivity content in the "Pietra di Modica" stone and radiological health risk assessment: a case study

Proceedings of the «2024 IEEE INTERNATIONAL CONFERENCE ON Metrology for Archaeology and Cultural Heritage (METROARCHAEO)»





$$C (Bq kg^{-1} d.w.) = \frac{N_E}{\epsilon_E t \gamma_d M}$$

		Specific activity	
Sample	C <sub>Ra</sub> (Bq kg <sup>-1</sup> d.w.)	C <sub>Th</sub> (Bq kg <sup>-1</sup> d.w.)	C <sub>K</sub> (Bq kg <sup>-1</sup> d.w.)
Pietra di Modica	36.1 ± 6.1	2.2 ± 0.5	20.2 ± 3.8

$$I = (C_{Ra}/300 + C_{Th}/200 + C_{K}/3000)$$

$$Ra_{eq} (Bq kg^{-1}) = C_{Ra} + 1.43C_{Th} + 0.077C_{K}$$

$$H_{ex} = (C_{Ra}/370 + C_{Th}/259 + C_{K}/4810)$$

$$H_{in} = (C_{Ra}/185 + C_{Th}/259 + C_{K}/4810)$$

Sample	I	Ra <sub>eq</sub> (Bq kg <sup>-1</sup> )	H <sub>ex</sub>	H <sub>in</sub>
Pietra di Modica	0.14	41	0.11	0.21



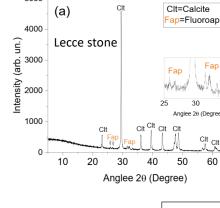


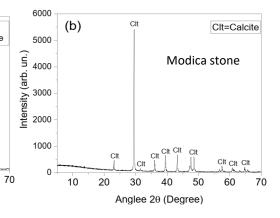




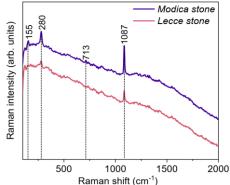
4. G. Faggio, G. Messina, D. Chiriu, S. Da Pelo, M. Guida, D. Majolino, M. Ponte, S.A. Ruffolo, V. Venuti, F. Caridi **Comprehensive Analysis of Lecce and Modica Stones Using X-Ray Diffraction and Raman Spectroscopy**Proceedings of the «2024 IEEE INTERNATIONAL CONFERENCE ON Metrology for Archaeology and Cultural Heritage (METROARCHAEO)»



















## Participation at conferences

- I. 4<sup>th</sup> International Workshop on "MOdelling, SImulation and Data Analysis in Engineering and Physics Applications" (MOSIDA 2024) within The International Conference on Applied Physics, Simulation and Computing (APSAC 2024). <u>Invited talk</u> "Assessment of the radon exhalation and the radiological risk due to natural radioactivity content in the "Pietra di Lecce" building material: a case study" Roma, 20 22 June 2024
- 2. 2024 IEEE INTERNATIONAL CONFERENCE ON Metrology for Archaeology and Cultural Heritage (MetroArchaeo). <u>Talk</u> "Natural radioactivity content in the "Pietra di Modica" stone and radiological health risk assessment: a case study"
  - <u>Talk</u> "Comprehensive Analysis of Lecce and Modica Stones Using X-Ray Diffraction and Raman Spectroscopy" <u>Poster</u> "Comparison of the Radon Exhalation Rate of building materials of particular historical and artistic interest: preliminary results on Ignimbrite Campana, Modica stone and Mendicino stone" *Valletta Campus, Malta, 07-09 October 2024*









# https://athena.unime.it/

